The Inevitability of Engine-Out NOx Emissions from

Spark-Ignition and Diesel Engines

P.F. Flynn, G.L. Hunter, L.A. Farrell, R.P. Durrett, O.C. Akinyemi, A.O. zur Loye,
Cummins Engine Co., Columbus, IN, 47202, USA

and

C. K. Westbrook and W. J. Pitz
Lawrence Livermore National Laboratory, Livermore, CA, 94550 USA

Abstract

Spark-ignition and Diesel engine combustion experiments were carried out for fuels including natural gas, propane and indolene, showing that flame extinction and high unburned hydrocarbon emissions result when in-cylinder combustion temperatures fall below a critical threshold value of approximately 1920K. Laminar flame calculations were then carried out for methane and propane to relate these experimental limiting temperatures to those associated with lean limit conditions for flame propagation. Model laminar flame results for pressures above 50 atm. produced a lean limit at an equivalence ration of 0.6, where the adiabatic flame temperature was about 1900K. These results show that at the elevated pressures of engine combustion, the lean-limit product temperature for these hydrocarbon fuels is considerably higher than that obtained previously for lean-limit flames at atmospheric pressure and that these much higher temperatures will produce significant amounts of NO_X. These coupled studies indicate that under conditions of pressure and temperature in both spark-ignition and Diesel internal combustion engines, high product gas temperatures are required and relatively high NO_X production rates are the inevitable result. Thus it may be impossible to reduce NO_X production to very low levels if flame propagation at high pressures is involved, and it will be necessary to provide post-combustion after-treatment to reduce NO_X emissions to legislated levels.

Introduction

Internal combustion engines, both spark ignition and Diesel, are dominant types of vehicle power sources and also provide power for other important stationary applications. Overall, these engines are a central part of power generation in modern society. However, these engines, burning hydrocarbon fuels from natural gas to gasoline and Diesel fuel, are also responsible for a great deal of pollutant emissions to the environment, especially oxides of nitrogen (NO_X) and unburned hydrocarbons (UHC).

In recent years, pollutant species emissions from internal combustion engines have been the object of steadily more stringent limitations from various governmental agencies. Engine designers have responded by developing engines that reduce emissions to accommodate these tighter limitations. However, as these limits become ever more stringent, the ability of engine design modifications to meet those limits must be questioned.

Production of NO_X in internal combustion engines is primarily due to the high temperature extended Zeldovich reaction mechanism:

$$O + N_2 = NO + N \tag{1}$$

$$N + O_2 = NO + O \tag{2}$$

$$N + OH = NO + H \tag{3}$$
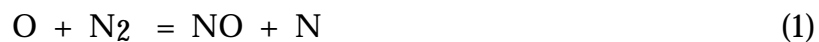
The rates of these reactions become significant when combustion temperatures reach or exceed about 2000K. This large temperature dependence, characterized by large activation energies for the rates of the reactions listed here, is a direct result of the need to break apart the tightly bonded oxygen and nitrogen molecules. The strongest bond is the triple bond in the $N \equiv N$ molecule, resulting in an activation energy of about 75 kcal/mole for Reaction (1), which is the principal cause for the large temperature dependence of the extended Zeldovich NO_X mechanism. In most engines, NO_X is therefore produced primarily in the high temperature combustion product gases.

Figure 1 illustrates how temperatures such as those existing in the combustion zones of heavy-duty engines produce NO_X emissions. Chemical evolution of reaction products from combustion of a fuel/air mixture at an equivalence ratio of 0.65 was computed using a reaction mechanism based on GRI-Mech [1] and the Miller/Bowman [2] NO_X mechanisms. These calculations, intended to estimate characteristic rates of NO_X production, were carried out at fixed temperatures and a fixed pressure of 100 bar, and the curves in Fig. 1 show computed results at residence times of 1 and 5 msec. This equivalence ratio is similar to that of a heavy duty lean-burn spark-ignition or diesel engine. From Fig. 1, at temperatures of about 2000K and residence times of 1 – 5 msec, which are typical of residence times at these temperatures in engines, the production of

NO_X increases dramatically. In an engine, the total amount of NO_X produced is therefore a function of the amount of mass that reaches these high temperatures.

Experimental results

The experimental parts of the present study were not originally conceived as a coherent, focused research activity. The data summarized here are the results of many years of engine studies that were intended to explore many features of combustion near the lean limits of combustion in both spark-ignition and Diesel engines. The spark-ignition engine experiments were carried out on various heavy-duty engines with displacements from 1.0 to 3.1 liters per cylinder, and the Diesel experiments were also carried out in a variety of different engines. Combustion temperatures were found to be of particular importance in interpreting the experimental results, but these temperatures are difficult to extract from these experimental studies. Appropriate models must be used to determine relevant temperatures, and these are subject to uncertainties that must be examined. Furthermore, the overall conclusions of this study do not require exceptional accuracy in determination of temperatures, and depend more on trends in the variations of flammability limits and extinction temperatures with pressure and equivalence ratio.

Spark-ignition engine experiments

Experiments were conducted to determine how lean a spark-ignition

engine could be operated to minimize NO_X production while still maintaining

reasonable fuel economy. In addition to controlling the level of NO_X emission, it

was important that combustion be complete in order to minimize exhaust

unburned hydrocarbons. As fuel/air ratios were leaned or as combustion timing

was retarded, circumstances were encountered where unburned hydrocarbons

rose drastically even though the engines continued to run steadily and NO_X

emissions were lowered. This suggested that flame propagation near the end of

the combustion process was weakened in the cases where the temperature rise in

the flame was low enough that combustion could not be completed.

Figure 2 presents these circumstances. Plotted in this diagram are the

unburned hydrocarbon emissions of the engine on a fuel-specific basis against

the end-of-combustion flame temperatures. The results in Fig. 2 represent values

with propane as the fuel, but very similar results were obtained for other fuels as

well. The end-of-combusstion temperatures were estimated using a constant

pressure, adiabatic calculation at the equivalence ratio at which the engine was

operating. The starting temperature for this temperature rise calculation was the

adiabatically compressed end gas temperature at the point where 95% of the total

heat release had occurred. These are "engine-out" values prior to any

aftertreatment. Note that at 100 g/kg, unburned hydrocarbons represent 10% of the entire fuel in the engine.

This diagram shows that if the flame temperatures are allowed to fall too low during the combustion process, a very substantial fraction of the total fuel is not burned and the combustion process will not be completed. The limiting end-of-combustion flame temperature was determined to be approximately 1900K, as illustrated in Fig. 2. This was the first data in this study that suggested that there might be a possible temperature limit for the combustion of hydrocarbons inside engines. Realistic estimates of the accuracy of these temperatures are $\pm$ 50K or even somewhat higher.

Some years ago, Smith et al. [3] studied essentially the same problem of flame quenching in an expanding combustion chamber. At lean values of equivalence ratio ($\phi \sim 0.6$), they determined that when the combustion chamber had expanded to reduce the adiabatic flame temperature below about 1606K, the flame would be quenched. The pressure ranges for the experiments of Smith et al. were only slightly greater than atmospheric and considerably lower than the approximately 50-100 atmospheres of the present study, indicating an increase in flame quenching temperature with increasing pressure. As noted below, Law and Egolfopoulos [4] computed a quench temperature of about 1460K at one atmosphere pressure, consistent with the present results. Smith et al. commented that bulk quenching became increasingly important as the ignition timing is retarded, also consistent with the evidence from the experiments

described above. The same type of flame quenching phenomenon was observed

by Quader [5], with a similar explanation.

These experiments show that engine expansion leads to a condition in

which the product temperature falls below a critical value, effectively quenching

further combustion, and that all the fuel remaining unburned at this time would

be observed as UHC emissions. At lower values of the equivalence ratio, the

flame speed is further reduced and combustion takes even longer to complete, so

a smaller amount of expansion and cooling is needed to extinguish the flame.

On exploring the circumstances portrayed in Fig. 2 in more detail, it was

concluded that if such a minimum temperature limit did exist, its ramifications

would be observable under other kinds of circumstances. If 1900K is a real

minimum temperature for flame propagation, it ought to be impossible to start a

flame before circumstances were created that would give a flame temperature

above 1900K.

Figure 3 depicts the results of a series of experiments designed to test this

premise. In these experiments, a variety of typical and high energy ignition

systems were installed on an engine with spark timings set at unrealistic

advanced settings. The focus of the experiments was to see if there was a

discernable limit in terms of flame temperatures required for combustion to be

initiated. The "burned zone" temperature was determined by adding the

adiabatic flame temperature rise for the existing equivalence ratio to the

adiabatically compressed end gas temperature when the first significant heat release was observed.

As indicated in Fig. 3, no flames were observed with a post-reaction burned zone temperature less than about 1900K. These experiments were run with several ignition systems. One of the peculiar circumstances observed was that with very high energy ignition systems and very early spark timings, the spark could be set off early under circumstances such that flame propagation did not occur immediately; however, flame propagation would then be initiated later in the compression stroke once the lean reactants had been compressed to the point where the burned zone temperature had reached the 1900K threshold. That is, the total heat release and associated temperature increase of the reactants hadn't changed, but now the gases had been compressed enough that the sum of the temperature rise from reaction and the temperature increase due to compression had reached 1900K. .

Similar circumstances were observed in engines running on propane, natural gas, and indolene. The limiting temperatures observed over this range in fuels have been nearly invariant. These observations are consistent with those of Badr [6], Hertzberg [7] and others. This similarity of quench temperature with different hydrocarbon fuels is evidently caused by the fact that the final energy release from any alkane hydrocarbon fuel comes from the oxidation of similar small fuel fragments.

Both series of spark-ignition engine studies provide a consistent picture of a flammability limit where the combustion temperature must exceed 1900K for flame propagation to be possible. The important new feature of the present study is that these results were all obtained at engine pressures considerably greater than atmospheric pressure, sometimes approaching 50-100 atmospheres. It is also clear that the combustion temperatures are not particularly well specified, so the actual limiting value of 1900K is somewhat uncertain from the experiments, although they are accurate to within approximately $\pm$ 50K.

Diesel engine experiments

Additional experiments to assess the operational characteristics of practical engines near limits of flammability were carried out over a number of years in conventional Diesel engines to which progressively more and more cooled exhaust gas recirculation (EGR) was added to the air intake manifold. The engine operated with 75 psi bmep and at constant fuel injection rate and injection timing.

The addition of inert diluent has several effects on combustion, including a gradually lower average temperature, longer duration of combustion, lower total heat release, lower NO_x production, and finally rapid rises in unburned hydrocarbons, CO and soot production. An attempt was made to determine if it

was possible to interpret these results in a manner similar to those obtained above from the spark-ignition engine results.

In a Diesel engine, it is difficult to define a combustion temperature that is comparable to that in a premixed environment. In the Diesel, most of the combustion takes place in a diffusion flame where the temperature is considerably greater than elsewhere in the combustion chamber. Extracting the peak combustion temperatures from experimental data is dependent on modeling the diffusion flame as well as identifying a way to calibrate experimental measurements from the combustion. For this study, experimental data on radiation from the Diesel flame, combined with a simple model of a diffusion flame [8], was used to compute a peak flame temperature for the interpretation of the engine data. However, the values for the flame temperatures computed in this way should be interpreted as only approximate, due to the many simplifications involved in the simple model.

The results of a complete series of nine experiments with varying EGR are shown in Figures 4 and 5, in which the fuel-specific NO_x production is plotted against peak flame temperature and brake-specific fuel consumption. As expected, the NO_x falls almost to zero as the peak flame temperature is decreased to about 2000K, but the fuel consumption increases rapidly as the NO_x is reduced. Although not shown in Fig. 5, the increases in fuel consumption for

the last three, lowest NO_X points translated almost totally into increased soot

and UHC emissions. Thus these experiments show that as the peak flame

temperature in the Diesel engine falls below about 2150K and the NO_X levels

continue to decrease, hydrocarbon and soot emissions grow very rapidly. These

temperatures are not greatly different from the values developed above for

spark-ignition combustion. It should not be expected that critical flame

temperature for premixed flame propagation should be exactly the same as that

for diffusion flames, and estimations of the flame temperatures in the Diesel

experiments are more uncertain than those in the spark-ignition engine. The

main point is that both types of flame propagation seem to have critical

combustion temperatures that are reasonably similar and are quite close to

temperatures where NO_X production would be expected to proceed at a

significant rate.

All of these experimental results for spark-ignition and Diesel engine

combustion were interpreted in terms of a flammability limit to combustion. In

the next section, recent theoretical and modeling studies of lean flammability

limits are used to examine these experimental results and their implications for

pollutant emissions from these engines.


Lean flammability limits

Law and Egolfopoulos [4,9] studied the lean limit of flame propagation for laminar flames of hydrogen, mixtures of hydrogen and CO, and a variety of small hydrocarbon species in air at atmospheric pressure and room temperature. They found that this limit was characterized by a competition between the primary chain branching reaction

$$H + O_2 = O + OH \tag{4}$$

and the related reaction

$$H + O_2 + M = HO_2 + M \tag{5}$$

At lean conditions approaching the flammability limit, reaction (5) not only suppresses chain branching, but it effectively provides chain termination, since the HO_2 produced then often reacts with OH

$$HO_2 + OH = H_2O + O_2 \tag{6}$$
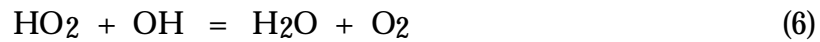
to make stable, unreactive species. Reaction (4) provides chain branching because it consumes one H atom radical and produces two new radical species. In contrast reaction (5) consumes the same H atom radical and produces one HO_2 radical, making it a chain propagation reaction. When reaction (6) follows reaction (5) the overall path consumes one radical and produces none, making it a chain termination sequence.

The rate expressions for reactions 4 and 5 are:

$$k_4 = 5 \times 10^{16} \ T^{-0.82} \ \exp(-16500/RT)$$

$$k_5 = 1.65 \times 10^{15} \ \exp(+1000/RT)$$

Because of the large difference in activation energies for these two reactions, the relative rate of the quenching reaction (5) will increase relative to the rate of reaction (4) as temperature is reduced. Flame temperatures decrease monotonically with decreasing equivalence ratios for lean fuel/air mixtures. Therefore, for laminar flames at atmospheric pressure, Law and Egolfopoulos showed that, as the equivalence ratio is decreased, reaction (5) steadily begins to compete with the chain branching reaction (4), and at the lean limit, the rate of reaction (5) actually equals the peak rate of reaction (4) in the flame. This occurs at an equivalence ratio of $\phi \cong 0.48\pm0.02$ for methane/air, in good agreement with experimental observations [10,11] that the lean limit is found at approximately $\phi = 0.5$. For even lower values of the equivalance ratio, the excess chain termination due to reaction (5) effectively quenches the flame. Law and Egolfopoulos also noted that at the lean limit of $\phi \cong 0.48\pm0.02$ the adiabatic flame temperature was about 1460K for methane/air at atmospheric pressure. Approximately the same lean limit flame temperature was noted for other hydrocarbon fuels at atmospheric pressure, although the lean limit flame temperature for hydrogen/air was found to be about 1000K for hydrogen/air, also at atmospheric pressure. Law and Egolfopolous also noted that the lean

limit flame temperature increased rapidly for flames with significant heat losses included in the model calculations.

We have repeated the same type of laminar flame calculations as those of Law and Egolfopoulos but at the compressed gas temperatures and pressures that we expect to see under engine conditions. Specifically, we selected conditions with pressure of 50 atm and corresponding unburned gas temperature of 650K. This is a slightly higher compression than most spark-ignition engine combustion and a moderately lower compression than most Diesel engine combustion, but it provides an illustrative set of conditions. We carried out model calculations for methane and propane; the experimental results suggest that results for other hydrocarbon fuels would be very similar.

A return to the discussion above of the rates of reactions (4) and (5) shows that reaction (4) is bimolecular while reaction (5) is termolecular, meaning that the rate of reaction (5) increases with pressure relative to the increase in the rate of reaction (4), at a constant temperature. Thus one would expect that at elevated pressure, reaction (5) will compete with reaction (4) at higher temperatures and correspondingly greater equivalence ratio. Calculations of laminar flames at elevated pressure were then carried out to test this assumption and to predict the magnitude of the effect of increased pressure on the lean limit.

The Chemkin laminar flame model was used to compute the flame speed and spatial variations in species concentrations and temperature through the flame. A chemical kinetic reaction mechanism was used that had been

developed for and tested by comparisons with a wide variety of experimental combustion data [12-14]. At 650K and 50 atm, using exactly the same basis for the properties of the lean flammability limit as used by Law and Egolfopoulos, we found that the peak rate of reaction (5) reached the rate of reaction (4) at the center of the flame when the equivalence ratio ϕ reached a value of about 0.6. At these conditions, the adiabatic flame temperature was about 1900K. Both of these values are subject to some uncertainty, depending on details of the chemical kinetic reaction mechanism, the specific rate expressions for reactions (4) and (5), and other details of the laminar flame model. However, the results clearly indicate that the lean flammability limit at elevated pressures occurs at an adiabatic flame temperature much higher than that at atmospheric pressure, and the flammability limit at elevated pressure can be associated with flame temperatures in the vicinity of 1900K.

These changes in the adiabatic flame temperature and the limiting equivalence ratio with pressure and temperature are shown to be directly related to the competition between the rates of reactions (4) and (5). The pressure dependence of the rate of reaction (5) makes it compete with the rate of reaction (4) at higher temperatures as the pressure is increased.

The rate of reaction (5) does not increase strictly proportionately with pressure over the pressure range from 1 to 50 atm. Like many such reactions, eventually increases in pressure are not fully reflected in an increased reaction rate. Kineticists refer to this effect as "pressure falloff" and results in a somewhat

slower response of the reaction rate to pressure increase than might initially be expected. We have included the pressure dependent rate of reaction (5) due to pressure falloff in our computations. If we had not included the falloff effects in the reaction rate, the changes in lean limit equivalence ratio and adiabatic flame temperature with pressure would have been even greater than those reported here.

The combination of the experimental observations and the computed lean limit laminar flame conditions show that at elevated pressures, the requirements of flame propagation ensure that adiabatic flame temperatures must exceed values that are of the order of 1900K or greater. In fact, if the flame temperatures at the beginning and end of combustion are equal or greater than 1900K, it is clear that during the remainder of the engine combustion cycle, temperatures will be considerably greater than 1900K for normal operation. Typical variations in temperatures during the combustion period suggest that maximum temperatures would be expected to be higher than the minimum values by about 300 – 400 K during the combustion period. At such temperatures, the rate of production of oxides of nitrogen (NO_X) will be significant, as shown in Fig. 1.

The implications of these computations are important. These computations have shown that if the adiabatic flame temperature of the combustible mixture is less than about 1900K at typical engine conditions, then the mixture will not burn. However, at and above such temperatures, the rate of

NO$_X$ production is significant and will lead unavoidably to appreciable

production of NO$_X$. Modifications in combustion processes cannot reduce NO$_X$

production below this level without serious misfire or other production of even

more significant hydrocarbon emissions. Thus the engine designer is faced with

a choice. The only way to reduce NO$_X$ emissions is to reduce flame temperatures

below about 2000K, but that will result in significant emissions of unburned

hydrocarbons. Consumption of the hydrocarbons requires temperatures high

enough to lead to significant production of NO$_X$. If environmental regulations

require NO$_X$ emissions below some especially demanding level, no in-cylinder

engine modifications will be able to satisfy those regulations, and the only way to

respond will be to provide aftertreatment to reduce the production of unburned

hydrocarbons that is the inevitable result of the low combustion temperatures.

  The present work is based on experience derived from many years of

analysis of piston-driven internal combustion engines. However, the results may

be more general; the combination of kinetic modeling of flame propagation and

qualitative experimental results indicate that any system in which the

combustion involved propagation of hydrocarbon/air flames at high pressures

(i.e., above 50 bar) would be subject to similar effects. Extension of this type of

analysis to systems such as gas turbines might therefore be warranted.

Conclusions

The chemical kinetic analysis and empirical results described in this paper clearly indicate that a limiting temperature exists for sustaining viable combustion for both lean-burn spark-ignition and diesel engine configurations presently used in heavy-duty applications. At the pressures typical of both spark-ignition and diesel engines (i.e., 50 – 100 bars), the limiting temperature is of the order of 1900K. Above this temperature, NO_x production is significant, while below this limit, significant emissions of unburned hydrocarbons are the result. This limiting temperature for combustion viability leads directly to a limit in the potential for NO_x reductions in-cylinder. Since regulators are proposing NO_x emissions levels significantly below these limiting in-cylinder values, these regulations will require combinations of in-cylinder combustion management plus the adoption of very effective, long lived NO_x and hydrocarbon removal engine aftertreatment systems. To date none of these aftertreatment systems has demonstrated the capabilities for high efficiency, long life and broad range operation that will be demanded in the future.

In the present work, engines were run under pathological conditions, far from normal operations, to see what characteristics were observed that might be common to failing combustion. Spark ignition engines were operated under conditions where late spark and piston expansion forced flame quench. In

addition, spark ignition engines were operated with too lean a mixture to

complete combustion in time, and spark ignition engines were operated with too

much spark advance before the mixture was flammable. Diesel engines were

operated with too much EGR to maintain stable operation. For all of these

problems, the one common feature was that all had 1900-1920K in common as

the limit to flame propagation.

References

1. Bowman, C. T., Hanson, R. K., Davidson, D. F., Gardiner, Jr., W. C., Lissianski, V., Smith, G. P., Golden, D. M., Frenklach, M., and Goldenberg, M., *http://www.me.berkeley.edu/gri_mech/*,1995.

2. Miller, J. A., and Bowman, C. T., Prog. Energy Combust. Sci. 15, 287-338 (1989).

3. Smith, O. I., Sawyer, R. F., and Westbrook, C. K., Seventeenth Symposium (International) on Combustion, pp. 1305-1313, The Combustion Institute, Pittsburgh, 1978.

4. Law, C. K., and Egolfopoulos, F. N., Twenty-Fourth Symposium (International) on Combustion, pp. 137-144, The Combustion Institute, Pittsburgh, 1992.

5. Quader, A. A., "What Limits Lean Operation in Spark Ignition Engines: Flame Initiation or Propagation?" Society of Automotive Engineers publication SAE-760760, 1976.

6. O.A. Badr, N. Elsayed and G.A. Karim, Journal of Energy Resources Technology, Transactions of the ASME, Vol. 118, pp. 159-163 (1996).

7. Martin Hertzberg, The Flammability Limits of Gases, Vapors and Dusts: Theory and Experiment, Proceedings of the International Conference on Fuel-Air Explosions, University of Waterloo Press, Waterloo, Ontario (1982).

8. Primus, R. J., unpublished engine correlation model, 1990.

9.   Law, C. K., and Egolfopoulos, F. N., Twenty-Third Symposium (International) on Combustion, pp. 413-421, The Combustion Institute, Pittsburgh, 1990.

10.   Andrews, G. E., and Bradley, D., Combustion and Flame \

11.   Coward, H. F., and Jones, G. W., "Limits of Flammability of Gases and Vapors", Bureau of Mines Bulletin 503 (1952).

12.   Westbrook, C. K., and Pitz, W. J. **Combustion Science and Technology** 37, 117-152 (1984).

13.   Curran, H. J., Gaffuri, P., Pitz, W. J., and Westbrook, C. K. **Combustion and Flame** 114, 149-177 (1998).

14.   Curran, H.J., Pitz, W.J., Westbrook, C.K., Callahan, C.V., and Dryer, F.L., **Twenty-Seventh Symposium (International) on Combustion**, pp. 379-387, The Combustion Institute, Pittsburgh, 1998.

Figure captions

1. Computed production rates of oxides of nitrogen at different residence times.

2. Hydrocarbon emissions as functions of flame temperatures, for spark ignition engines.

3. Correlation of flame temperature with spark timing, for spark ignition engines.

4. NO_X emissions as functions of peak flame temperatures.

5. Correlation of NO_X emissions with fuel consumption.